

MOISTURE CROSSLINKABLE THERMOPLASTICS IN THE MANUFACTURE OF VEHICLE WEATHER STRIPS

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The present application is a continuation-in-part application of U.S. Serial No. 09/912,099, filed July 24, 2001.

BACKGROUND OF THE INVENTION

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The present invention relates to a process for forming composite extrusions and the products formed thereby, particularly automobile weather strips. More particularly, the present invention pertains to vehicle weather strip composite extrusions comprised of an elastomeric thermoset and a crosslinked thermoplastic polyolefin.

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It is common in the motor vehicle industry to fashion decorative abrasion resistant sections for various parts of an automobile by extruding such sections from certain thermosetting polymeric materials. Examples of typical abrasion resistant sections manufactured by such a process include colored weather strips. These weather strips are mounted on an automobile door surface and

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along the perimeter of automobile doors to provide a seal between the door and the automobile body as well as to protect both the door and exterior objects when they come in contact with each other. Weather strips are typically extruded and attached to a vehicle by an adhesive tape.

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Various thermoset elastomeric rubber materials, such as ethylene propylene diene terpolymer (EPDM), styrene-butadiene copolymer (SBR) and chloroprene rubbers have been used to form these weather strips. These materials are favored by manufacturers because they are relatively inexpensive compared to thermoplastics and generally exhibit both the desired flexibility necessary for providing an effective seal and acceptable weatherability

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properties. However, these elastomers typically lack the low-friction, abrasion resistance that is necessary at the point of contact with exterior objects for extended life of the weather strips.

Manufacturers have therefore attempted a variety of approaches to improve the wear resistance and other properties of elastomeric sealing sections. One strategy for weather strips has been to apply a second layer of low friction polymer to the surface of the elastomeric weather strip along the area that is exposed to the exterior. Incorporated within the second layer can be various pigments or dyes such that the surface of the weather strip matches the color of the automobile. Depending on the composition of the main body of the weather strip, this second layer is often formed from polyvinyl chloride (PVC) or an uncured non-polar thermoplastic elastomer, such as polypropylene or polyethylene. These second layers are usually applied directly to the weather strip surface by lamination or as a solvent-based spray, or after an application of a primer or adhesive layer to the elastomer. However, these methods are not completely satisfactory. In addition to longer processing time and added material cost, it is difficult to obtain a satisfactory bond between the elastomer and the surface coating. Sprayed on coatings are prone to cracking while an adhered layer is susceptible to peeling.

Another method that manufacturers have used to adhere the second layer to the extruded weather strip is to cohesively bond a layer of wear resistant thermoplastic to the weather strip. Several techniques have been developed to accomplish this. According to one method, the elastomer rubber and the second layer are co-extruded. The resulting composite is then passed through an oven in which the elastomer rubber is cured and the interface between the second layer and the rubber is heated to such a degree that the second layer partially melts, causing it to adhesively bond with the rubber. Alternately, the rubber is extruded first and passes through an oven in which it is at least partially cured. A molten thermoplastic is then extruded onto the vulcanized rubber. The residual heat of the rubber as it emerges from the oven promotes interdiffusion of the two layers at the interface between the two, forming a bond between the two materials.

Due in part to the uncrosslinked nature of the thermoplastic, however, it is difficult to control exactly the degree of melting that the second layer undergoes in this technique. If the second layer melts too much, the abrasion resistance it affords will be compromised and its aesthetic appeal

diminished. Thus, there is a need for a new vehicle weather strip composite that overcomes the deficiencies and limitations of the prior art.

BRIEF SUMMARY OF THE INVENTION

5 The present invention provides a process for forming an extruded automobile weather strip comprising a main body member of elastomeric rubber and an abrasion resistant decorative layer, the abrasion resistant decorative layer comprising a crosslinkable thermoplastic polyolefin ("TPO") including a crosslinkable olefinic homopolymer and a crosslinkable ethylene- α -olefin
10 copolymer or ethylene-styrene interpolymers. The use of a crosslinkable TPO allows a manufacturer to maintain the desirable qualities associated with thermoplastics while affording greater control of melting and alleviating other processing concerns. In a preferred embodiment, the elastomeric rubber is EPDM and the crosslinkable TPO is a two component composition including a
15 moisture curable ethylene- α -olefin copolymer or a crosslinkable copolymerized ethylene-styrene interpolymers modifier in a moisture curable polyethylene or polypropylene homopolymer matrix. The crosslinkable components may contain grafted silane functional groups. In the presence of moisture, water hydrolyzes the silane. Under the action of a catalyst, the resulting silanol groups then
20 condense to form intermolecular crosslinking sites. The thermoset elastomer rubber may be cured by sulfur or peroxide agents. The crosslinkable TPO can be applied to the elastomer rubber main body member by extruding the material directly onto the rubber or by extruding the material into a tape form and applying the tape to the EPDM by means of a laminating technique.

25 The versatility of crosslinkable TPO's allows them to be applied to the elastomer rubber member in several ways. In a first preferred technique, the crosslinkable TPO is co-extruded with an uncured thermoset elastomer rubber main body member and then exposed to water to crosslink the copolymer. The resultant composite is then passed through an oven to vulcanize the thermoset
30 elastomer rubber. In a second preferred technique, the crosslinkable TPO is step extruded onto a previously cured or partially cured thermoset elastomer rubber main body member and then crosslinked by immersion in a water bath, or otherwise exposed to moisture. In a third preferred technique, the

crosslinkable TPO is extruded into a sheet or tape form and laminated onto a previously cured or partially cured thermoset elastomer rubber main body member. The resulting composite is then subjected to a water bath, or otherwise exposed to moisture, to crosslink the grafted silane groups.

5 While all the techniques produce acceptable results, if the crosslinkable TPO is applied to the thermoset elastomer prior to the curing of the elastomer, the thermoplastic should be crosslinked before the elastomer is cured. This is to ensure that the TPO does not melt excessively during the subsequent heating.

10 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross section of a preferred embodiment weather strip for a vehicle in accordance with the present invention.

Figure 2 is a depiction of a first preferred technique of the present invention for manufacturing a composite extrusion suitable for use as weather
15 strip for a vehicle.

Figure 3 is a depiction of an alternative preferred technique of the present invention for manufacturing a composite extrusion suitable for use as a weather strip for a vehicle.

Figure 4 is a depiction of an another alternative preferred technique of the present invention for manufacturing a composite extrusion suitable for use as a
20 weather strip for a vehicle.

Figure 5 is a flowchart depicting the main processing steps in the first preferred technique of the invention detailed in figure 2.

Figure 6 is a flowchart depicting the main processing steps in the second preferred technique of the invention detailed in figure 3.
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Figure 7 is a flowchart depicting the main processing steps in the third preferred technique of the invention detailed in figure 4.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

30 The present invention provides a variety of sealing strips and weather strips for vehicles. Briefly, the weather strips preferably comprise at least two components, each formed from particular materials and having a unique cross-sectional configuration. A preferred weather strip comprises a thermoset

elastomer rubber main body member having any of several shapes conventional in the art.

The weather strip also comprises an abrasion resistant decorative layer comprised of an abrasion resistant material disposed on the outwardly facing surface of the main body member. As explained in greater detail below, the layer preferably comprises a moisture crosslinkable TPO including a moisture crosslinkable ethylene- α -olefin copolymer or a crosslinkable copolymerized ethylene-styrene interpolymer and a moisture crosslinkable olefin homopolymer polymeric resin.

With reference to figure 1, a cross-section of a preferred embodiment weather strip for a vehicle in accordance with the present invention is shown. The preferred embodiment weather strip is comprised of a main body member 2, made from one or more of a number of elastomeric thermoset rubbers known in the art to be suitable for weather strip applications, and an abrasion resistant decorative layer 4.

Suitable elastomeric rubber compositions for use in the main body member include, but are not limited to, ethylene- α -olefin-non-conjugated diene rubbers (EODM), styrene-butadiene rubbers (SBR), acrylonitrile-butadiene rubber, natural or synthetic isoprene rubber and chloroprene rubber. EODM rubbers are preferred due to their oxygen, ozone and weather resistance. Suitable α -olefins include, but not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene and 1-decene. A preferred α -olefin is propylene. A preferred group of EODM compounds suitable for the present invention are ethylene-propylene-diene terpolymers (EPDM). Suitable non-conjugated dienes include, but not limited to, 1,4-hexadiene, dicyclopentadiene and 5-ethylidene-2-norbornene. A preferred EODM for the main body member of the weather strip of the present invention is ethylene-propylene-ethylidene-norbornene terpolymer or ethylene-propylene-dicyclopentadiene terpolymer. Various grades of elastomer thermoset rubber may be used in the invention including dense elastomers and less dense, sponge elastomers.

The elastomer rubber of the main body member can further include various additives known in the art in such concentrations that do not adversely affect the properties of the compound. Such additives include, but are not

limited to, vulcanization agents, carbon black, lubricants, plasticizers, fillers, slip agents, processing oils and antioxidants. These additives are added to the elastomer prior to extrusion.

In one preferred embodiment (figure 1), the main body member **2** is formed having a hollow tube **6** joined along its longitudinal axis at a region **8** on its outer circumference to a tangential wall **10**. Attached to one end of the tangential wall is a retention spur **12**. Attached to an opposite end of the tangential wall is a second wall **14**. The second wall **14** is substantially perpendicular to the tangential wall **10** at the junction between them, but gently curls back toward the tangential wall as the second wall **14** extends from the tangential wall **10**. The second wall **14** terminates at and defines its distal end **16** as shown in figure 1. Approximately midway between the junction of the tangential wall **10** and the second wall **14**, and the distal end **16** of the second wall **14**, a third wall **18** substantially parallel to the tangential wall **10** extends from the second wall **14**. Together, the tangential wall **10**, the second wall **14** and the third wall **18** define an interior chamber **20**. Projecting from the tangential wall **10** on an opposite side from the hollow tube **6** are a plurality of sealing lips **22** that extend inward and upward therefrom toward the interior chamber **20**. Attached to a distal end **24** of the third wall **18** and projecting inward and upward therefrom toward the interior chamber **20** is a large sealing lip **26**. Depending on the make of the automobile and the shape of the chassis and doorframe, many alternative embodiments are also contemplated.

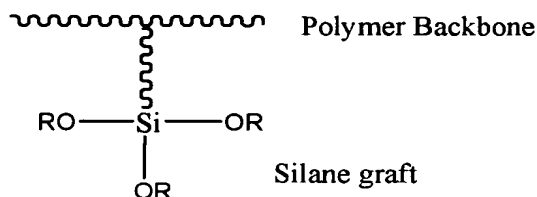
Irrespective of the exact shape of the main body member, extruded onto an exteriorly directed top surface (not numbered) of the second wall **14** of the main body member **2** is the abrasion resistant decorative layer **4** comprised of a crosslinkable TPO including at least two polymeric components. This abrasion resistant decorative layer **4** is applied along the main body member at those areas that contact the door, vehicle frame or exterior objects (not pictured) to improve the wear resistance and aesthetics of the weather strip at those locations. In addition, the abrasion resistant decorative layer **4** may be extruded onto other areas of the main body member **2** that contact these objects for added protection and scuff resistance, such as the various surfaces of the main body member (not numbered) that are exposed to and face the interior chamber **20**.

As explained in greater detail herein, in the final composite extrusion, such as incorporated into a door or window assembly, the at least two polymeric components of the TPO making up the abrasion resistant decorative layer are both at least partially crosslinked. Thus, although much of the description herein refers to the abrasion resistant decorative layer as comprising crosslinkable polymeric materials (as noted above), it will be understood that in its preferred final manufactured form, the composite extrusion of the present invention utilizes an abrasion resistant decorative layer that comprises at least partially crosslinked materials.

In a particular embodiment of the invention, the abrasion resistant decorative layer 4 is a two component TPO polymeric composition comprising a crosslinkable olefinic homopolymer and crosslinkable ethylene- α -olefin copolymer. Preferred crosslinkable olefinic homopolymers and crosslinkable ethylene- α -olefin copolymers are those that can be crosslinked by silane grafting. Electron beam radiation crosslinking is not preferred because of its expense. Likewise, peroxide crosslinking is not preferred because of the processing concerns that it entails. However, it is contemplated that the present invention weather strip and related methods could utilize such techniques for crosslinking. Preferred ethylene- α -olefin copolymers include silane grafted, metallocene catalyzed ethylene-butene, ethylene-hexene, ethylene-1-octene, and other ethylene alpha olefin copolymers. A most preferred ethylene- α -olefin copolymer for use in the present invention is silane grafted ethylene-octene copolymer.

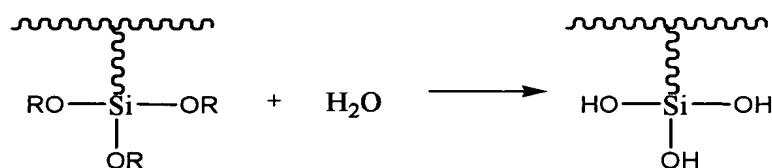
Preferred olefinic homopolymers for use in the TPO include silane grafted polyethylene, polypropylene, and higher olefin homopolymers. Most preferred homopolymers include silane grafted polyethylene and polypropylene. The homopolymers can be made via a variety of polymerization systems (including metallocene catalyzed and conventional catalysis systems) and have a range of molecular weights and other characteristics. In one preferred embodiment, the homopolymer is a polypropylene having a Mn of from about 20,000 to 100,000, a Mw of from about 50,000 to 200,000 and a molecular weight distribution of from about 2.5 to 4.0.

One stage silane crosslinking involves the extrusion of a direct mixture of the polymer resin with a silane concentrate that includes a catalyst. The extrudate is subsequently crosslinked in the presence of water. In two-stage crosslinking, silane is first grafted to the polymer molecular chains according to known reactions to yield a silane grafted copolymer.

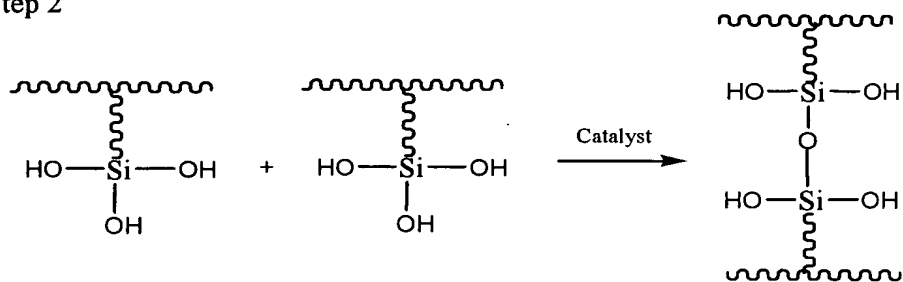


Subsequently, the silane-grafted copolymer is mixed with a silanol condensation catalyst and then exposed to water to effect crosslinking of the copolymer in a two step reaction. First, the water hydrolyzes the silane to produce a silanol. The silanol then condenses to form intermolecular, irreversible Si-O-Si crosslink sites.

Step 1



Step 2



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The amount of crosslinked silane groups, and thus the final polymer properties, can be regulated by controlling the production process, including the amount of catalyst used. A gel test (ASTM D2765) is used to determine the amount of crosslinking. Prior to being silane grafted, the ethylene- α -olefin

copolymer used in the invention preferably has a melt flow index determined according to ASTM D-1238 of about 0.5-50 g/10 min and a Shore A hardness of about 60-90. Most preferably, the ethylene- α -olefin copolymer used in the invention exhibits a melt flow index of about 5g/10 min at 230°C with a 2.16 kg
5 load, a Shore A hardness of about 70 and a density of about 0.8 - 1.2 g/cm³.

The catalyst can be any of a wide variety of materials that are known to function as silanol condensation catalysts including many metal carboxylates and fatty acids. A preferred catalyst is dibutyltindilaurate. The TPO preferably includes about 60% to about 95% by weight of the ethylene- α -olefin copolymer
10 and from about 5% to about 25% by weight of the olefin homopolymer. More preferably, the TPO includes about 70% to about 90% by weight of the ethylene- α -olefin copolymer and from about 5% to about 15% by weight of the olefin homopolymer. The crosslinkable TPO can also contain conventional additives including, but not limited to, organic and inorganic fillers, plasticizers, slip
15 agents, UV stabilizers, antioxidants and, as previously mentioned, coloring agents. Typical additives include talc in an amount up to about 10% by weight, and paraffinic and silicone oils up to about 10% by weight individually. A silane grafted ethylene-octene copolymer base resin suitable for use in the TPO of the present application is available from Collect LLC (formerly Sentinel Polyolefins)
20 under the trade name THERMOCHROME B® or from Dupont-Dow Elastomers LLC under the trade name ENGAGE®.

In a second preferred embodiment of the invention, the abrasion resistant decorative layer is comprised of a crosslinkable olefinic homopolymer matrix as described above modified with a crosslinkable copolymerized ethylene-styrene
25 interpolymer. This material is an interpolymer based on the copolymerization of ethylene and styrene. The interpolymer can have a styrene content of from about 30% to about 70%, preferably from about 30% to about 50% and more preferably about 40% and preferably exhibits a melt index prior to silane grafting of 1.6 g/10 min tested according to ASTM D1238. The interpolymer is
30 polymerized using a metallocene catalyst or other methods known in the art. In addition, other conventional additives can be added to the interpolymer without departing from the scope of the invention such as fillers, plasticizers, oils and pigments. A suitable interpolymer is available from the Dow Chemical Co. under

the trade name Index[®] Interpolymers. As with the ethylene-octene copolymer described previously, the interpolmer is silane grafted to allow it to be moisture crosslinked according to the reaction described above.

After crosslinking, the thermoplastic assumes many of the characteristics
5 associated with a thermoset, to a greater or lesser degree depending on the amount of crosslinking.

The abrasion resistant decorative layer **4** can be applied to the main body member **2** in one of several different ways. For ease of description, the different processes will be described utilizing a two stage crosslinkable, silane-grafted
10 ethylene-octene copolymer/polyethylene homopolymer as the abrasion resistant decorative layer **4** and EPDM as the thermoset elastomer rubber main body member **2**. However, the present invention contemplates the use of other crosslinkable polyolefins as well as an ethylene-styrene interpolmer as the abrasion resistant decorative layer **4** and other elastomers in the main body
15 member **2**.

The present invention provides a first preferred technique for producing a composite extrusion by co-extruding an uncured EPDM main body member, such as item **2** in figure 1, and an uncrosslinked silane-grafted ethylene-octene copolymer/polyethylene abrasion resistant decorative layer, such as item **4** in
20 figure 1, through an extrusion die. With reference to figure 5, a schematic diagram is shown outlining the preferred processing steps in this first preferred technique. Briefly, an uncured EPDM rubber and crosslinkable ethylene-octene copolymer/polyethylene are provided **500**, **502**. The EPDM rubber and the crosslinkable ethylene-octene copolymer/polyethylene TPO are coextruded **504**
25 to form a main body member and an abrasion resistant decorative layer, respectively. Subsequently, both the ethylene-octene copolymer and the polyethylene in the TPO are at least partially crosslinked **506**. The EPDM rubber of the main body member is then at least partially cured **508** prior to removal of the assembly from the processing line **510**.

With greater detail and with further reference to figure 2, a first extruder
30 **50** for processing a silane-grafted crosslinkable ethylene-octene copolymer/polyethylene compound, a second extruder **52** for processing a sponge EPDM and a third extruder **54** for processing a dense EPDM are placed

in communication with an extrusion die **56**. The term "sponge EPDM" refers to an EPDM that contains blowing agents. The term "dense EPDM" refers to an EPDM that does not contain any blowing agents. For ease of description, the production process will be described using the dense extruder **54**, although in
5 actual practice both are typically used concurrently, depending on the application. In order to ensure sufficient flow of the EPDM compound for subsequent extrusion, the EPDM extruder **54** is preferably maintained at a temperature of from about 70°C to about 85°C. For the same reason, the ethylene-octene/polyethylene extruder **50** is preferably maintained at about
10 130°C to about 210°C. The extrusion die **56** is preferably maintained at about 110°C on an EPDM side **58** and from about 200°C to about 260°C on an ethylene-octene/polyethylene side **60**. Insulation (not shown) between the two sides of the extrusion die allows for this disparity in temperatures to be more easily achieved. For a dense EPDM, the EPDM is extruded at a pressure of
15 from about 2000 to about 5000 psi, and most preferably about 4000 psi. For a sponge EPDM, the EPDM is extruded at a pressure of about 1000 psi to about 3000 psi, most preferably about 2500 psi. The ethylene-octene/polyethylene and EPDM are co-extruded such that the ethylene-octene/polyethylene layer mechanically bonds with the EPDM through molecular chain inter-diffusion and
20 entanglement. The thickness of the resulting ethylene-octene/polyethylene layer is preferably from about 0.1 to about 1.5 mm, and typically about 0.5 mm.

Referring further to figure 2, the composite extrusion (not shown) comprising the extruded EPDM and TPO is then passed through a steam bath **62** to effect crosslinking of both the polyethylene homopolymer and the
25 ethylene-octene copolymer. The steam bath **62** is preferably maintained at a temperature of from about 100°C to about 110°C. To cure the EPDM, the composite extrusion is then passed through an oven **64** or other curing device at a temperature of from about 180°C to about 270°C, depending on the grade of EPDM used in the main body member **2**. In a particularly preferred
30 embodiment, the composite extrusion is passed through a number of temperature zones in the oven **64** starting at about 200°C for about 15 to about 50 seconds, ramping up to about 220°C for about 45 seconds to about 2.4 minutes, and then ramping down to about 210°C for about 15 to about 50 seconds, prior to exiting the oven **64**. Preferably, the total oven cure time is

between about 1 minute and about 4 minutes. The composite extrusion is then cooled in a water or air cooling tank **66** at about 30°C to 90°C, and most preferably about 60°C, before removing the composite extrusion from the manufacturing line.

5 In a second preferred technique in accordance with the present invention, the uncured ethylene-octene/polyethylene TPO is extruded onto the main body member after the EPDM has been at least partially cured. With reference to figure 6, a schematic diagram is shown outlining the processing steps in this third preferred technique. Briefly, an EPDM rubber and crosslinkable ethylene-octene/polyethylene TPO are provided **600**, **602**. The EPDM rubber is extruded **604** into a main body member and the main body member is subsequently at least partially cured **606**. The crosslinkable TPO is extruded **608** as an abrasion resistant decorative layer onto the main body member. Both the ethylene-octene copolymer and the polyethylene homopolymer of the abrasion resistant
10 TPO layer are crosslinked **610** and then cooled prior to removal **612** of the assembly from the processing line.

 With additional detail and with further reference to figure 3, an extruder **52** for sponge EPDM and an extruder **54** for dense EPDM are placed in communication with a first extrusion die **70**. For ease of description, the
20 production process will be described using only the dense extruder **54**, although in actual practice both are typically used concurrently to make different sections of the same part. EPDM is extruded from the rubber extruder **54** through the first die **70** to form a main body member (not shown). The main body member is then passed through an oven **64** to cure the EPDM. Upon emerging from the
25 oven **64**, an abrasion resistant layer (not shown) comprising the above described TPO is extruded from a second die **72** that is fed by a plastic extruder **50** onto the cured main body member to form a composite extrusion. The residual heat of the EPDM main body member mechanically bonds the TPO therewith through diffusion. An embossing wheel **74** assists in bonding the
30 EPDM to the TPO by pressing the two layers together. In addition, the embossing wheel **74** may be used to print surface patterns on the composite extrusion (such as a "leather-like" texture). The composite extrusion is passed through a water cooling bath **62** to cool the composite and to crosslink the ethylene-octene copolymer and the polyethylene of the TPO prior to removal **76**

from the manufacturing line. The temperatures and pressures for the second technique are preferably similar to those used for the first technique in all respects except that the first die **70** is at a temperature from about 100°C to about 120°C, the second die **72** is at a temperature from about 200°C to about 220°C and the embossing wheel **74** is at a temperature from about 170°C to about 210°C, and preferably about 185°C.

In a third technique, an uncured TPO is extruded into a sheet and then laminated onto a cured EPDM main body member. With reference to figure 7, a schematic diagram is shown outlining the processing steps in this third preferred technique. Briefly, a thermoset elastomer rubber and the above described TPO are provided **700, 702**. The EPDM rubber is extruded **704** into a main body member and the TPO is extruded **706** into an abrasion resistant decorative sheet layer. The main body member is at least partially cured **708** and the sheet layer then laminated **710** onto the main body member. The sheet layer is then at least partially crosslinked **712** before the resultant assembly is cooled and removed **714** from the processing line.

With additional detail and with further reference to figure 4, an extruder **52** for sponge EPDM and an extruder **54** for dense EPDM are placed in communication with a first extrusion die **70**. As stated earlier, for ease of description, the production process will be described using the dense extruder **54**, although in actual practice both are typically used concurrently. EPDM from the rubber extruder **54** is extruded through the first die **70** into a main body member (not shown). The main body member is passed through an oven **64** to cure it. TPO is extruded from a second extruder **50** through a second die **82** to form an abrasion resistant layer in the form of a sheet **80**. An embossing wheel **74** then bonds the uncured TPO sheet **80** to the main body member to form a composite extrusion (not shown). The composite extrusion is then passed through a water bath **62** to crosslink the ethylene-octene copolymer and the polyethylene components of the TPO and to cool the composite prior to removal from the line **76**. The temperatures and pressures for the third technique are preferably similar to those used for the first technique in all respects except that the first die **70** temperature is from about 100°C to about 120°C, the second die **82** temperature is from about 200°C to about 220°C and the lamination wheel is at a temperature from about 170°C to about 210°C, and preferably about 185°C.

While various changes and adaptations may be made to the above methods without departing from the scope of the invention, it is important to note that, with regard to the first preferred technique described, the ethylene-octene copolymer is most preferably crosslinked prior to passing the composite
5 extrusion through the oven to avoid excessive melting of the uncrosslinked TPO.

The invention has been described with reference to various preferred embodiments. Obviously, modifications and alterations will occur to others upon a reading and understanding of the specification. The invention is intended to include all such modifications and alterations insofar as they come within the
10 scope of the appended claims and the equivalents thereof. Thus, for example, composite extrusions for other parts (such as automobile glass run channels) in addition to vehicle weather strips can be manufactured by the techniques of the present invention.